Adsorption of the Lighter Homologs of Element 104 and Element 105 on DGA Resin from Various Mineral Acids

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ADSORPTION OF THE LIGHTER HOMOLOGS OF ELEMENT 104 AND ELEMENT 105 ON DGA RESIN FROM VARIOUS MINERAL ACIDS

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Background

The goal of studying transactinide elements is to further understand the fundamental principles that govern the periodic table. The current periodic table arrangement allows for the prediction of the chemical behavior of elements. The correct position of a transactinide element can be assessed by investigating its chemical behavior and comparing it to that of the homologs and pseudo-homologs of a transactinide element. Homologs of a transactinide element are the elements in the same group of the periodic table as the transactinide. A pseudo-homolog of a transactinide element is an element with a similar main oxidation state and similar ionic radius to the transactinide element. For example, the homologs of rutherfordium, Rf, are titanium, zirconium and hafnium (Ti, Zr and Hf); the pseudo homologs of Rf are thorium, Th, and plutonium, Pu. Understanding the chemical behavior of a transactinide element compared to its homologs and pseudo-homologs also allows for the assessment of the role of relativistic effects.

Relativistic effects occur when the velocity of the s orbital electrons closest to the nucleus approaches the speed of light. These electrons approach the speed of light because they have no orbital momentum. This causes two effects, first there is in a decrease in Bohr radius of the inner electronic orbitals because of this there is an increase in particle mass[1, 2]. A contraction of outer s and p orbitals is also seen. The contraction of these orbitals results in an energy destabilization of the outer most shell, in the case of transactinides this would be the 5f and 6d orbitals. The outer most d shell and all f shells can also experience a radial expansion due to these orbitals being screened from the effective nuclear charge[2-5]. Another relativistic effect is the "spin-orbit splitting" for p, d and f orbitals into $j = 1 \pm \frac{1}{2}$ states[4]. Where j is the total angular momentum vector and l is angular quantum number. All of these effects have the same order of magnitude and increase roughly according to Z^2 [4]. This feature is what makes studying the heavy elements so interesting because the chemical properties of transactinide elements should strongly exhibit these effects. For this work the terms heavy element and transactinide elements will be used interchangeably and are defined as elements with an atomic number greater than 103, Z > 103.

In order to study the transactinide elements they must be isolated once they have been produced and transported to a chemistry apparatus. The transactinide elements are produced either via "hot" or "cold" fusion reactions. "Hot" fusion reactions result in excitation energies of the compound nucleus of 40 -50 MeV and occur when an actinide target nuclei fuse with a

projectile with A< 40, where A is the atomic mass number. "Cold" fusion results in excitation energies of 10 – 15 MeV. Cold fusion conditions tend to occur when a target of a spherical nuclei (Pb or Bi) is bombarded with a heavy projectile (A>40). Hot fusion generally leads to neutron rich isotopes and cold fusion tends to produce a compound nucleus that emits 1-2 neutrons upon de-excitation. If a sufficiently thin target is employed, then the products of the nuclear reaction will recoil out of the target and can either be transported to the chemistry setup, e.g. using a gas jet, or trapped by implementing them on a catcher. An example for a catcher setup using a copper block as a catcher is described here. The copper block is placed behind the target during the irradiation and all nuclei recoiling from the target position will implant themselves in the block. The copper block is subsequently dismounted and sputter cleaned. It is then shaved with a micro-lathe. The 7 – 10 μm copper shavings are then subjected to chemical separation[6]. The copper is dissolved in aqua regia. Lanthanum carrier is added to the aqua regia to precipitate tri-, tetra- and penta- valent cations when ammonium hydroxide is added. The precipitate is then washed and converted to the nitrate form. This solution is then added onto a cation exchange column, the eluent is deposited and dried on a polypropylene film and then counted on solid state detectors[7].

There are several challenges when studying the chemical behavior of transactinide elements. The first challenge is the low production rate of transactinides. Transactinides are produced on an atom-at-a-time basis, meaning that only one atom is ever available for chemical study. Because of this the chemical system being used must be selective for only one chemical state. The second challenge in transactinide chemistry is the short half-lives of the elements. Half-lives of the transactinides range from nanoseconds to a few hours. This leads to the need for fast chemistry. Another challenge is the need for a high degree of separation from interfering radionuclides so that the event with the transactinide element can be detected[5, 8]. Extraction chromatography lends itself very well to the needs of transactinide chemists because it provides rapid separation, high yields, large separation factors and requires only small volumes of solution.

Experiments and Methods

The goal of this project was to investigate the adsorption of the lighter homologs of rutherfordium, Zr and Ti, and the lighter homologs of dubnium, Nb and Ta, on DGA resin from

various mineral acids. DGA is an extraction chromatographic resin that is commercially available from Eichrom Technologies, Inc. The DGA resin consists of either N'N'N'N'-tetra-n-octyldiglycolamide or N'N'N'N-tetrakis-2'-ethylhexyldiglycolamide as the active component sorbed on an inert polymer substrate. The structure of DGA is shown in Figure 1[9]. Hydrochloric acid was chosen as mobile phase for the initial experiments. HCl solutions with concentrations ranging from 0.01 M to concentrated acid and containing the analytes of interest (Zr and Hf or Nb, and Ta) were used.
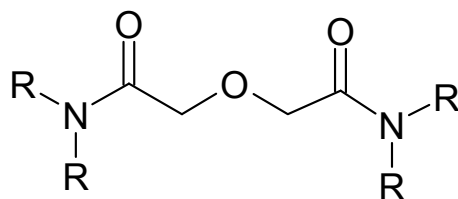
Figure 1. The structure of DGA where the R groups represent the straight or branched C8 chains.

Between 10 and 21 mg of DGA resin was placed in a 15 mL centrifuge tube. Then 1250 µL of Zr and Hf each, were placed in the centrifuge tube containing the DGA resin. The initial concentration of elemental solution added to the centrifuge tube was 1 ng/mL. This was then diluted to a total volume of 5 mL with a single acid concentration, resulting in a final concentration of 0.25 ng/ml for each element. The solution was then mixed on a vortex mixer for 2 minutes. The solutions were subsequently drawn into a 3 mL syringe and passed through a 0.45 µm filter before being transferred to a clean, dry 15 mL centrifuge tube. The filter was preconditioned with 3 mL of 6 M HCl. One syringe and one filter were used for an entire sample set. The solutions were extracted into the syringe in order from low to high acid concentration. The samples were then analyzed along with appropriate standard solutions to provide a calibration curve using inductively coupled plasma – mass spectrometry, ICP-MS. The instrument used was an Elan DRC II and the operational parameters utilized in this study are shown in Table 1.

**Table 1.** Operational settings for the Elan DRC II ICP-MS.

Parameter	Value
Nebulizer Gas Flow	0.96
Auxillary Gas Flow	1.20
Plasma Gas Flow	15.00
Lens Voltage	6.00
ICP RF Power Analog Stage Voltage	1100.00
Pulse Stage Voltage	-1562.00
Quadrupole Rod Offset Std	900.00
Cell Rod Offset Std	0.00
Discriminator Threshold	70.00
Cell Path Voltage Std	-11.00
RPa	0.00
RPq	0.25
DRC Mode NEB	0.92
DRC Mode QRO	-6.00
DRC Mode CRO	-0.50
DRC Mode CPV	-16.00
Cell Gas A	0.00
Cell Gas B	0.00

Results

A five-point calibration curve was measured for each element using varying amounts of stock solution ranging from 0 to 1250 µL. The calibration curves were necessary to not only quantify the amount of analyte the DGA extracted but also to monitor the performance of the ICP-MS. The percent of each element extracted by DGA was determined from a linear fit of the calibration curve, which is shown in Figure 2, and was normalized to a 1 mg of DGA Resin. This same procedure was performed for Nb and Ta.

The percent extracted by DGA for each element at all HCl concentrations investigated are shown in Table 1. The percent extracted by DGA at HCl concentrations ranging from 0.01 to 1 M are shown in Figure 3. The percent extracted at HCl concentrations ranging from 3 M to concentrated acid is shown in Figure 4. The large error bars are a result of the variation in counts

from the ICP-MS or possible kinetic effects. The kinetic effects could be reduced if longer mixing times are employed. Upon examination of Figures 3 and 4 it is immediately noticed that the DGA resin extracts no more than 10 % of Zr, Nb, Ta or Hf that was originally present in solution is sorbed to the DGA resin. The data also does not show an obvious relationship between acid concentration and amount sorbed. Evaluation of the data is hindered by the large variability shown for each data point. If Rf and Db behave similarly to their homologs then it is highly likely that very little of these transactinides will be retained by the DGA resin.
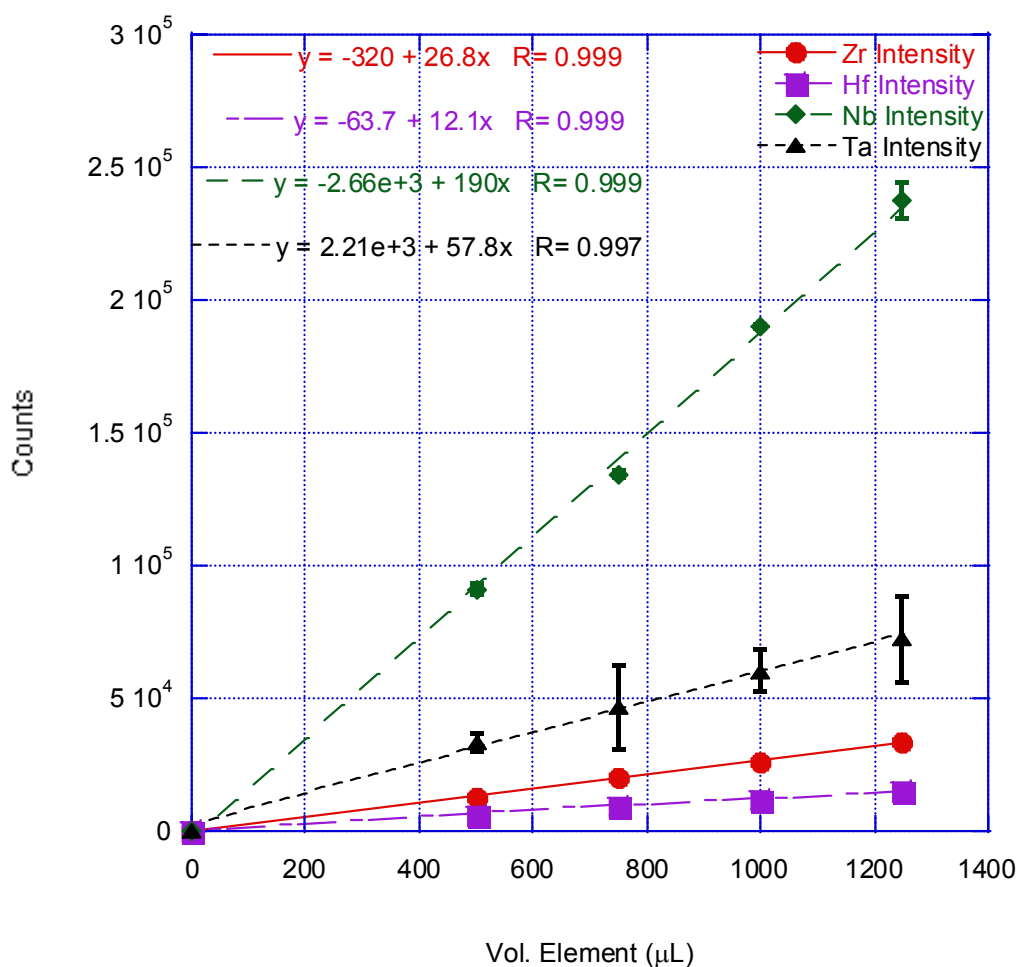
Figure 2. Example of a calibration curve used for the quantification of Zr, Hf, Nb and Ta.

Table 2. Percent of Each Element Adsorbed on DGA

| HCl [M]	Zr [%]	Hf [%]	Nb [%]	Ta [%]
0.01	5.65 ± 1.72	6.77 ± 7.74	5.55 ± 2.81	6.61 ± 2.92
0.1	6.31 ± 1.28	4.34 ± 1.98	6.91 ± 2.20	6.31 ± 2.23
0.3	5.45 ± 1.50	5.00 ± 1.69	5.38 ± 3.00	6.74 ± 0.89
0.6	6.16 ± 2.35	4.64 ± 1.92	4.81 ± 4.34	8.24 ± 1.43
1	5.40 ± 1.71	3.14 ± 1.99	5.41 ± 4.29	7.39 ± 1.95
3	6.54 ± 2.70	5.26 ± 4.76	4.33 ± 3.00	8.08 ± 0.89
6	5.74 ± 0.45	4.35 ± 0.71	___	6.84
8	6.30 ± 1.03	6.02 ± 0.64	5.21 ± 2.62	7.18 ± 0.95
10	7.06 ± 1.50	6.63 ± 1.71	5.05 ± 0.94	6.08 ± 1.18
12	7.26 ± 0.90	6.58 ± 1.27	6.77 ± 1.02	5.69 ± 1.32

Future Work

The investigation of the sorption behavior of natural Zr and Hf from various acid media on DGA resin will be completed. Solutions of sulfuric and nitric acid with concentrations ranging from 0.01 M to concentrated acid will be used as mobile phase. The extraction behavior will be assessed using ICP-MS. This study will also be completed for natural Nb and Ta. In addition the dependence of analyte concentration on extraction behavior the effect of carrier-free radioactive isotopes of Zr, Nb and Hf. The extraction of ^{95}Zr, ^{95}Nb and ^{175}Hf will be studied for selected acid concentrations. The percentage of activity sorbed to the resin will be determined by gamma ray spectroscopy.

In addition the DGA resin column durability and performance will be assed by performing successive loading and stripping steps with the same amount. Finally, the bleeding of the active component from the resin will be studied via HPLC-ES-MS studies.
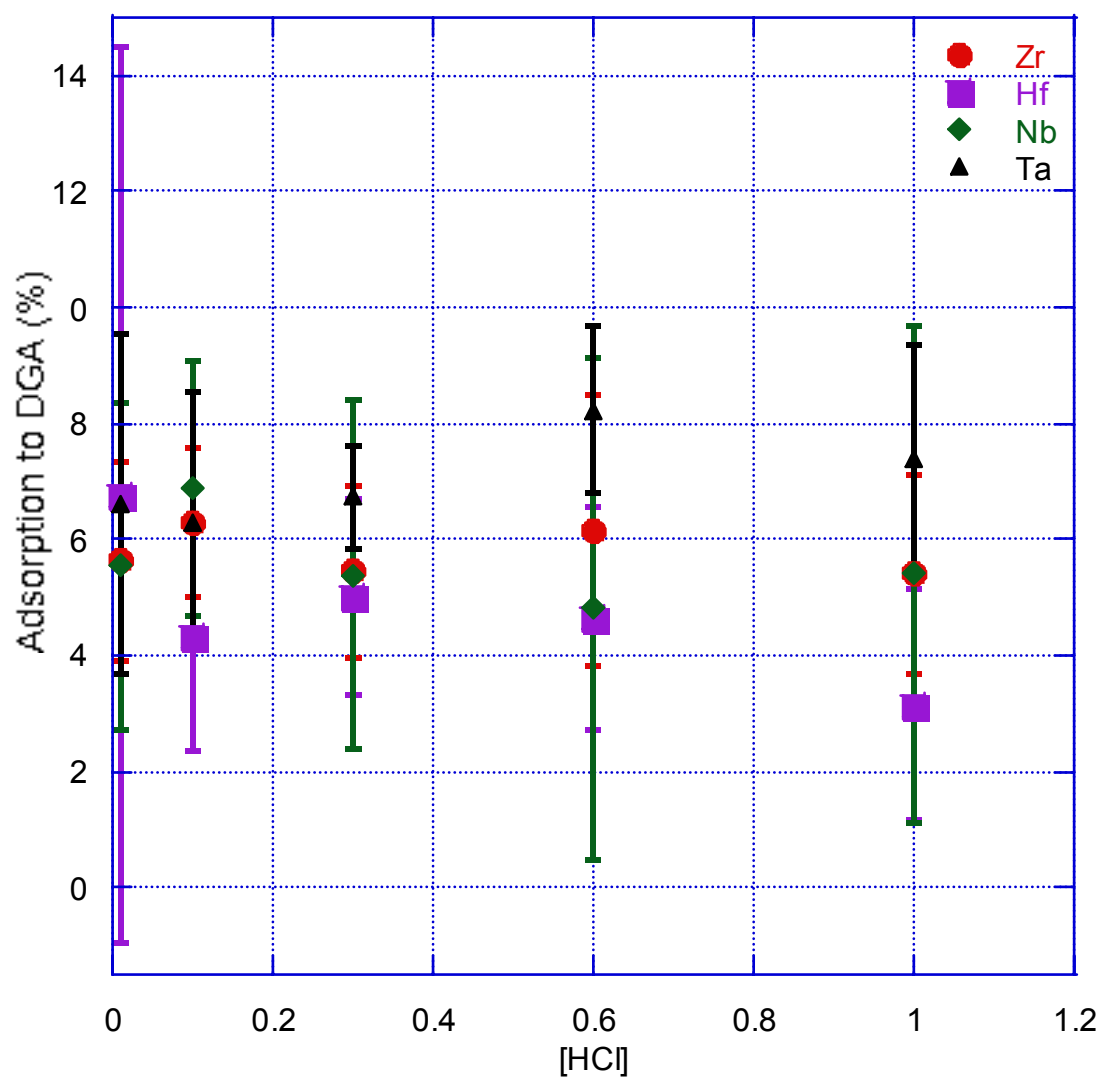
Figure 3. The percent of each element extracted by DGA from various hydrochloric acid solutions with concentrations ranging from 0.01 to 1 M.
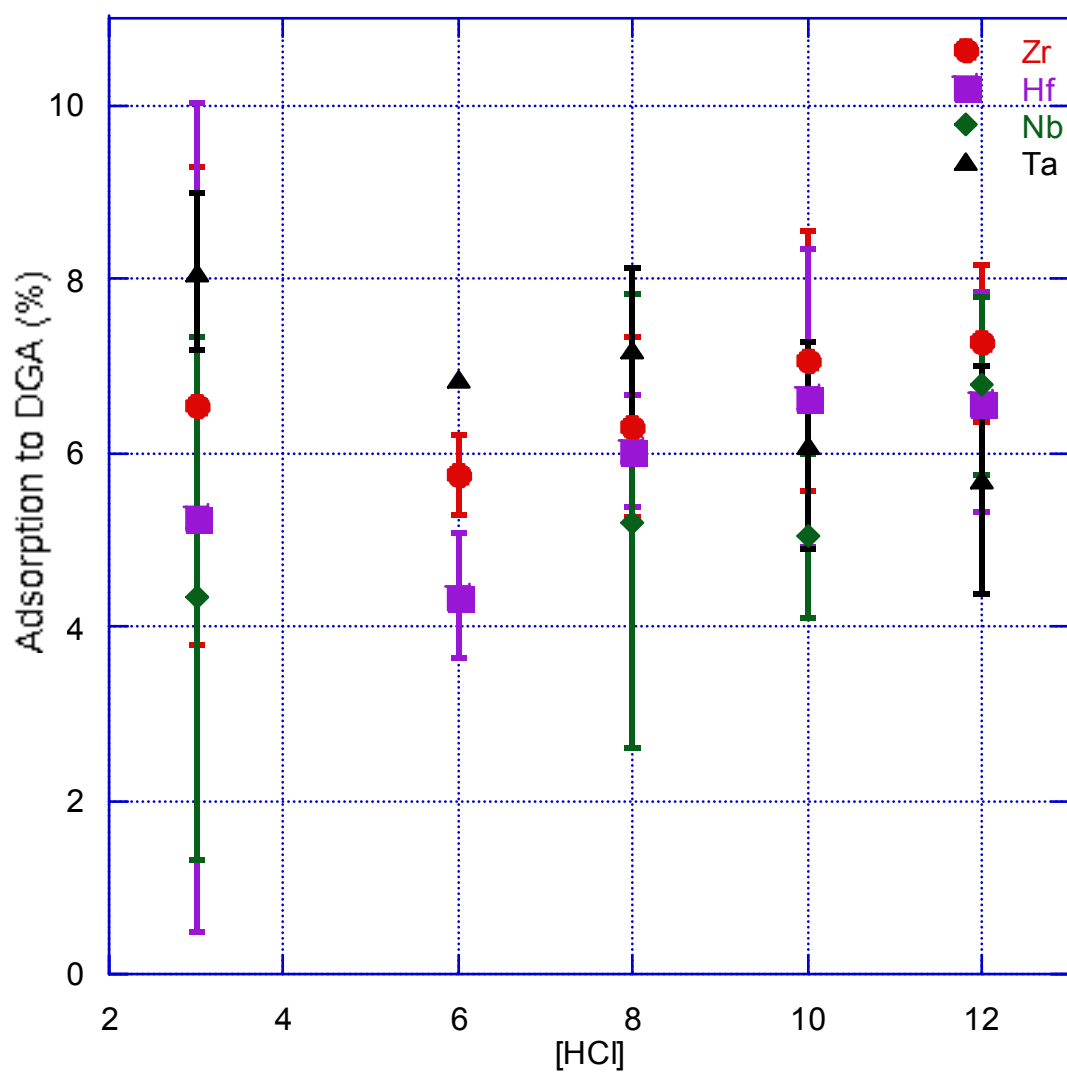
Figure 4. The percent of each element extracted by the DGA resin from various hydrochloric acid solutions with concentrations ranging from 3 to 12 M.

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